

II. "On the Surface Forces in Fluids." By A. M. WORTHINGTON. Communicated by Professor B. STEWART, F.R.S.
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(Abstract.)

The object of the paper is to deduce from consideration of the known thermal and elastic properties of fluids, the fact that at their bounding surface there is a rapid variation of density, on account of which the surface layers exert either a tension or a pressure on any material wall which cuts them transversely, from which action the phenomena of capillarity are easily deduced; and to exhibit clearly the manner in which the intrinsic energy per unit of volume of the surface layers exceeds or falls short of that in the interior of the fluid, and also to point out a certain important change which it is necessary to introduce into the commonly accepted explanation of the equilibrium of a fluid in contact with a solid; and, finally, to show why the erroneous assumption of a constant density near the surface, made by Laplace, did not prevent his obtaining the true equation to the liquid surface, while it did prevent him from perceiving the reality of the surface-tension.

The first step is to examine the significance of statical theories of molecular equilibrium, and to show that a statical theory, if framed in accordance with the observed phenomena of expansion of the substance with heat, and of its elastic resistance to compression or extension, is really equivalent to a statistical description of any internal dynamical phenomena that are taking place. The value of Poisson's "repulsive force of heat" as a statical representation of the rate of transfer of molecular momentum, or of the internal pressure within the substance, is pointed out, and the nature of the equilibrium between this force and the force of molecular attraction is examined.

The relation of the two forces may be advantageously exhibited by means of a diagram of two curves drawn to rectangular co-ordinates, whose horizontal abscissæ represent the intra-molecular distance, and whose vertical ordinates represent in each case the corresponding value of the force. It is shown that the equilibrium of the substance is stable only when the tangent to the curve of repulsion slopes more steeply than the tangent to the corresponding point of the attraction curve, and the difference between the ordinates to the two curves corresponds to the ordinate of an isothermal curve for the same substance as usually drawn.

The equilibrium of a non-volatile liquid, whose plane surface is exposed to a vacuum, is then studied in the following manner:—

The molecules are supposed at first to be distributed at the equal

distances apart, at which they may be supposed to be situated in the interior of the liquid, at some given temperature in nature. They are then supposed to be endowed with the attractive forces which (on a statical theory) they may be supposed to possess in nature, and the value of the repulsive heat-force or internal pressure is sought which is requisite to maintain the existing uniform density. It is found that this value increases with the depth up to the limit of the radius of molecular activity, after which it remains constant, and that consequently if such a uniform temperature be assigned to the substance as shall maintain the existing density of the interior molecules, a readjustment of the surface molecules will take place, involving an expansion of the surface liquid and an absorption of heat by it, from which it is seen that the surface liquid is in a condition to which the interior liquid would be reduced by stretching it, and may be regarded as a portion of the liquid on which heat energy has been spent in doing work against the molecular attractions.

The same treatment is then extended to the more general case, first of a liquid in contact with an incompressible and inextensible substance; then to two liquids in contact; and then to the contact of a liquid with its own vapour; and finally, to the contact of a fluid and a solid; with the result that at the surface of contact of two fluids the surface layers of each differ from the interior fluid by being in a state either of tension or pressure, and that the forces which are the subject of measurement in experiments on capillarity are the algebraic sum of the two sets of forces belonging to the two fluids respectively. If this resultant sum is a pressure, then the surface is unstable and its extension involves a dissipation of energy.

In the case of a liquid in contact with a gas or its own vapour, it is shown that the liquid is rarefied at the surface while the gas or vapour is condensed, but that there is a limit, for temperatures below the critical point, to the rarefaction possible to the one, and to the condensation possible to the other, and that the two limits are not coincident, and that consequently up to this point the phenomena of a surface-tension are presented, while above the critical temperature the two limits disappear simultaneously. The relation of this interpretation of the critical temperature to the suggestion of Professor James Thomson, made in his paper, "*Proc. Roy. Soc.*," vol. 20, p. 1, in reference to the continuity of the fluid state of matter, is pointed out.

In the case of the contact of a solid with a fluid it is only the surface forces of the latter that can produce any motion, and when one of the fluids is a gas above its critical temperature, it is shown that the surface force must be a pressure, whence it follows that a liquid which spreads over a solid in air must really be condensed on its surface, and the surface force must be a pressure, and not a tension, as usually supposed—a result which is arrived at in a different

manner by Maxwell ("Encyc. Brit.," art. "Capillarity"), and which is probably of importance when considered in reference to the solution of a solid in a liquid.

The influence of the curvature of the surface is then considered, and the connexion between the hydrostatic pressure and the repulsive and attractive forces that have been spoken of is pointed out, after which the relation of the investigation to that of Laplace is examined, and it is shown that in assuming the density to be invariable, Laplace obliges himself to neglect the very quantities from whose mutual relation, established by experiment, the reality of the surface-tensions and surface-pressures can alone be deduced.

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